

## Introduction to Debye Temperature and Heat Capacity

In this experiment, you will use a remarkably simple apparatus to demonstrate an important quantum mechanical effect which shows up when you are dealing with solids at low temperatures. To obtain decent results, you will need to plan carefully and be patient and methodical about taking data. Careful work can give results within a few percent of the predictions of quantum theory, while sloppy work will give poor results.

When considering the specific heat at constant volume for one mole of  $N$  atoms in a solid,  $C_v = dU/dT$ , you need to consider the energy  $U$  contained in the solid. Classically, each of the  $N$  atoms in the solid can be thought of as an independent oscillator executing simple harmonic motion about its lattice site in 3 dimensions, giving  $3N$  total degrees of freedom. According to energy equipartition, each degree of freedom is assigned an average energy of  $kT$ , where  $T$  is the temperature of the solid. In this model, then, the total energy is  $U = 3NkT$  and  $C_v = 3Nk = 3R = 6$  cal/mol/K, which is a constant.

At high temperatures this works well (and a roughly constant  $C_v$  was in fact measured for a range of substances when this model was proposed), but it was soon discovered that at low temperatures, this model fails, with  $C_v \rightarrow 0$  as  $T \rightarrow 0$  and  $C_v \sim T^3$ . In reality, instead of having  $N$  independent oscillators, there are actually  $N$  strongly coupled oscillators exhibiting  $3N$  coupled vibrations, since the atoms are connected to each other (not unlike masses connected by springs). This is a very complicated situation and difficult to solve.

Fortunately, Debye took a modified approach to the problem and was able to successfully model the situation. From a behavioral standpoint, the set of  $3N$  coupled vibrations from the  $N$  atoms is exactly like a set of three-dimensional standing wave modes of longitudinal vibration at a range of possible discrete frequencies (which represent the  $3N$  modes). The Eisberg and Resnick text describes it by saying that the modes of the longitudinal vibration of the solid as a whole (called phonons), with each mode independent of the others like the case of independent modes of coupled pendula, give the same individual atom motions as the actual coupling. So in the model Debye replaced the atoms with elastic vibrational modes of the whole solid, which are independent and non-interacting and can therefore be more easily analyzed. The modes are also distinguishable from each other since they can each be characterized by unique mode numbers  $n_x$ ,  $n_y$ , and  $n_z$  in 3 dimensions.

The analysis then proceeds like the analysis used to determine the photon energy in a cavity from blackbody radiation, with the exception that there is some maximum frequency  $\nu_m$  that needs to be considered when summing the allowed frequency modes for the solid (there is no such limit when considering the photons in a cavity). The total number of modes summed up to the limiting

frequency  $\nu_m$  must add up to  $3N$ , the number of degrees of freedom of the solid, which equals the number of possible modes. With this constraint and with the assumption that the boundaries of the solid are vibrational nodes,  $\nu_m$  can then be solved for in terms of the fundamental properties of the solid (these properties determine the allowed vibrational modes):  $\nu_m = v(9N/4\pi V)^{1/3}$  (note that  $T$  doesn't come into play here since the number of degrees of freedom =  $3N$  doesn't depend on  $T$ ).

Another way of thinking about this maximum frequency limit  $\nu_m$  for the allowed vibrational (phonon) modes in the solid is to realize that the corresponding minimum wavelength of the vibration,  $\lambda_m = v/\nu_m = (4\pi V/9N)^{1/3}$ , is comparable to the mean interatomic separation in the solid. It is not meaningful to think of a wave of atomic displacements with a wavelength less than the atomic separation (just think of beads on a string for an analogy to this...). Therefore we have a physical limitation ( $\nu_m$ ) on how high the frequencies can go in the solid, which corresponds to the  $3N$  limit on the number of modes.

When you are considering a solid at low temperatures, the energy of this high-frequency cutoff  $\nu_m$  is much higher than the accessible vibrational energy states of the phonons (since  $T$  is so low), and the frequency cutoff  $\nu_m$  never comes into play. In this case, you have the same situation as with the cavity photons (effectively no upper limit on the vibrational frequency is imposed) and you obtain an energy density in the solid which scales as  $T^4$ , in accordance with the Stefan-Boltzmann law which describes the energy density of photons in a cavity! The specific heat is then  $C_v = dU/dT \sim T^3$ , which is the behavior seen for the low temperature solid.

The temperature which corresponds to the energy of the highest frequency of allowed modes ( $\nu_m$ ) in the solid is called the Debye temperature,  $\theta$ , and is defined as  $\theta = h\nu_m/k$ . As described above,  $\nu_m$  is completely dependent on measurable quantities of the solid (and not dependent on  $T$ ) and so an estimate for  $\theta$  for a given substance can be determined empirically directly from the solid. The general mathematical expression for  $C_v$  as a function of  $T$  in the Debye model contains an integral with limits involving  $\theta$  (the integral is not solvable analytically), so by measuring  $C_v$  for a range of  $T$ , it is possible to fit the data to the model and try to estimate  $\theta$  indirectly. In principle you could compare your fitted result for  $\theta$  from the  $T$  and  $C_v$  measurements with an estimate from the measurable quantities of the solid and see how they compare.